

MEMORY DEVICE

BACKGROUND OF THE INVENTION

The present invention relates to memory devices whose memory cells include
5 capacitors using capacitive films made of ferroelectrics.

FIG. 5 shows a known memory device in which each memory cell is made of a capacitor using a ferroelectric for its capacitive film and a selective transistor selectively making the capacitor accessible. As shown in FIG. 5, one electrode of a ferroelectric capacitor **101** is connected to the source of a selective transistor **102** and the other
10 electrode is connected to a cell plate line **CP**. The drain of the selective transistor **102** is connected to a bit line **BL** and the gate thereof is connected to a word line **WL**.

FIG. 6 shows an example of a cross-sectional structure of a memory cell having such a circuit configuration. As shown in FIG. 6, the selective transistor **102** includes: drain and source regions **111** and **112** formed in an upper portion of a silicon substrate **110**
15 to be spaced from each other; and a gate electrode **114** formed over the substrate **110** and covered with a first insulating layer **113**.

The ferroelectric capacitor **101** is formed on the first insulating layer **113** and over the source region **112** and includes a first electrode **115**, a ferroelectric film **116** and a second electrode **117**.

20 The first electrode **115** of the ferroelectric capacitor **101** is electrically connected to the source region **112** of the selective transistor **102** via a first contact plug **118** provided through the first insulating layer **113**. The second electrode **117** of the ferroelectric capacitor **101** is connected to a cell plate line **CP**.

A second insulating layer **119** is formed on the first insulating layer **113** to cover
25 the ferroelectric capacitor **101**. A third insulating layer **120** is formed on the second

insulating layer **119** to cover the cell plate line **CP**.

A bit line **BL** is provided on the third insulating layer **120** and over the drain region **111**. The bit line **BL** is electrically connected to the drain region **111** via a second contact plug **121** formed through the first, second and third insulating layers **113**, **119** and **120**.

5 FIGS. **7A** through **7C** schematically show respective process steps of a method for forming the ferroelectric capacitor **101**. In FIGS. **7A** through **7C**, the selective transistor **102** is omitted.

First, as shown in FIG. **7A**, a first electrode film **115A**, a ferroelectric film **116** and a second electrode film **117A** are deposited in this order over a first insulating layer **113**.
10 Subsequently, a resist mask **130** is formed to cover a capacitor region on the second electrode film **117A**. Then, the second electrode film **117A**, the ferroelectric film **116** and the first electrode film **115A** are subjected to plasma etching using the resist mask **130**, thereby patterning a ferroelectric capacitor **101**.

However, the known memory device has a problem that, in a plasma etching
15 process in the fabrication process thereof, an etching atmosphere containing a large amount of active species such as reactive free radicals creates, in an end portion of the ferroelectric film **116**, a damaged region **116a** which is damaged by the active species and can no longer have any property as a ferroelectric.

The damaged region **116a** reduces the effective area of the ferroelectric capacitor
20 **101**. Specifically, the damaged region **116a** inwardly extends several tens nm to several hundreds nm from the side face of the ferroelectric film **116**. In the case where the area of the ferroelectric capacitor **101** is smaller than $1\ \mu\text{m}^2$, the reduction of effective area of the ferroelectric capacitor **101** cannot be neglected.

To suppress the occurrence of such a damaged region **116a**, recovery annealing for
25 recovering the damaged region **116a** is performed after the formation of the ferroelectric

capacitor **101**. However, this annealing cannot eliminate the damaged region **116a** completely.

In addition, the recovery annealing is performed at substantially the same temperature as the temperature at which the ferroelectric film **116** is crystallized.

5 Accordingly, if the ferroelectric capacitor **101** is a stack of a plurality of layers, the recovery annealing needs to be performed on each of the layers, so that wiring provided in each of the layers disadvantageously deteriorates with heat. As a result, it is difficult to achieve a three-dimensional capacitor array in which the ferroelectric capacitor **101** is a stack of two or more layers.

10 Moreover, in the known fabrication method, the ferroelectric film **116** is formed on the entire surface of the first electrode film **115A** by a sputtering method or a sol-gel method in the process step shown in FIG. **7A**, and therefore, polycrystallization is essential. Accordingly, the crystal orientation of each individual grain in this polycrystalline film would take an arbitrary direction. As a result, a significant fraction of
15 crystal grains would have little contribution to the polarization which can align along the applied electric field for polarization reversal.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to prevent a damaged region from
20 occurring in a capacitive film made of a ferroelectric. It is also an object of the present invention to prevent the polarization from appearing in different directions so as to control the crystal orientation.

In order to achieve the objects, the present invention provides a structure in which a ferroelectric film to be a capacitive film is selectively grown on a lower electrode.

25 Specifically, an inventive first memory device includes: a memory cell with a

capacitor including a first electrode, a ferroelectric film and a second electrode, which are formed in this order over a substrate, wherein the ferroelectric film is selectively grown on the first electrode.

5 In the first memory device, if the first electrode has been patterned into a desired shape, etching for patterning the ferroelectric film is not needed because the ferroelectric film is selectively grown on the first electrode. As a result, no damaged region is created in the ferroelectric film to be a capacitive film of a capacitor, so that the capacitor can be downsized.

10 In the first memory device, the ferroelectric film is preferably made of a single crystal or a single domain. Then, there occurs no variation in polarization direction due to uniformization of the crystal orientations in polycrystallization, thus making it possible to control the crystal orientation of the ferroelectric film such that the polarization is at the maximum.

15 In the first memory device, the ferroelectric film is preferably grown to be self-organized by physical or chemical interaction between the ferroelectric film and the first electrode. Then, the ferroelectric film can be formed on the first electrode with an arbitrary planar shape, being self-aligned thereto.

In the first memory device, the ferroelectric film is preferably grown in a vapor phase or in a liquid phase.

20 In the first memory device, the capacitor is preferably connected to a selective switching device. Then, in the case where a plurality of memory cells are arranged in an array, a desired cell can be easily selected from among the memory cells.

In this case, the selective switching device is preferably formed on the substrate or between the substrate and the first electrode. Then, the density in the arrangement of the
25 memory cells can be increased.

In this case, the selective switching device is preferably a transistor or a bidirectional diode. Then, if the selective switching device is a transistor, the memory cell array can be configured as an active matrix array. On the other hand, if the selective switching device is a bidirectional diode, the memory cell array can be configured as a simple matrix array.

An inventive second memory device includes: a first capacitor array layer including a plurality of capacitors each including a first electrode, a first ferroelectric film and a second electrode which are formed in this order over a substrate; and a second capacitor array layer including a plurality of capacitors each including a third electrode, a second ferroelectric film and a fourth electrode which are formed in this order as viewed from the substrate, the second capacitor array layer being formed over the first capacitor array layer with an insulating film interposed between the first and second capacitor array layers, wherein the first ferroelectric film is selectively grown on the first electrode, and the second ferroelectric film is selectively grown on the third electrode.

In the second memory device, the ferroelectric films included in the first capacitor array layer and the ferroelectric films included in the second capacitor array layer stacked on the first capacitor array layer are selectively grown on the first and third electrodes, respectively. Therefore, no etching for patterning the ferroelectric films is needed. As a result, no damaged region is created in the ferroelectric films to be capacitive films of the capacitors, so that the capacitors can be downsized. In addition, the capacitor array layers are disposed three-dimensionally, so that the density in the arrangement of memory cells can be increased.

In the second memory device, each of the first and second ferroelectric films is preferably made of a single crystal or a single domain.

In the second memory device, the first ferroelectric film is preferably grown to be

self-organized by physical or chemical interaction between the first ferroelectric film and the first electrode, and the second ferroelectric film is grown to be self-organized by physical or chemical interaction between the second ferroelectric film and the third electrode.

5 In the second memory device, each of the first and second ferroelectric films is preferably grown in a vapor phase or in a liquid phase.

 In the second memory device, the capacitors constituting the first and second capacitor array layers are preferably respectively connected to selective switching devices, thereby forming respective memory cells.

10 In this case, each of the selective switching devices is preferably formed on the substrate or between the substrate and the third electrode. Then, the wiring distance between the capacitor and the selective switching device in each of the memory cells is reduced.

 In this case, the selective switching devices are preferably transistors or
15 bidirectional diodes.

 In this case, the selective switching devices respectively connected to the capacitors constituting the second capacitor array layer are preferably formed in the second capacitor array layer.

 In this case, the selective switching devices formed in the second capacitor array
20 layer are preferably thin film transistors or bidirectional diodes.

 In this case, means for electrically connecting the memory cells included in the second capacitor array layer to one another is preferably provided between the first and second capacitor array layers or on the second capacitor array layer. Then, the density in the memory cell array in which memory cells are arranged three-dimensionally can be
25 further increased.

In this case, means for electrically connecting the memory cells included in the first capacitor array layer to the memory cells included in the second capacitor array layer is preferably provided between the first and second capacitor array layers. Then, the density in the memory cells in which memory cells are arranged three-dimensionally can be further
5 increased.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view showing a structure of a memory cell array which is a main portion of a memory device according to a first embodiment of the present
10 invention.

FIGS. 2A and 2B are cross-sectional views schematically showing respective process steps of a method for forming capacitive films of capacitors constituting the memory device of the first embodiment.

FIG. 3 is a graph for comparing the hysteresis characteristics of capacitors
15 constituting the memory device of the first embodiment to the hysteresis characteristics of known capacitors.

FIG. 4 is a cross-sectional view showing a structure of a three-dimensional memory array which is a main portion of a memory device according to a second embodiment of the present invention.

20 FIG. 5 is a circuit diagram showing a known memory device whose memory cells include ferroelectric capacitors.

FIG. 6 is a cross-sectional view showing a structure of the known memory device whose memory cells include the ferroelectric capacitors.

FIGS. 7A through 7C are cross-sectional views showing respective process steps of
25 a method for forming the known ferroelectric capacitors.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EMBODIMENT 1

A first embodiment of the present invention will be described with reference to the
5 drawings.

FIG. 1 shows a cross-sectional structure of a memory cell array which is a main portion of a memory device according to the first embodiment.

As shown in FIG. 1, a plurality of transistor regions divided by a plurality of transistor separation regions **11** made of silicon oxide are formed in an upper portion of a
10 semiconductor substrate **10** made of, for example, silicon. In the transistor regions, selective transistors **15** serving as selective switching devices are respectively formed. Each of the selective transistors **15** includes: source and drain regions **12** and **13** formed to be spaced from each other; and a gate electrode **14** formed over the semiconductor substrate **10** between the source and drain regions **12** and **13**.

15 A first insulating layer **16** is formed on the entire surface of the semiconductor substrate **10** including the transistor separation regions **11** and the gate electrodes **14**. First contact plugs **17** are formed through the first insulating layer **16** to reach the respective source regions **12**, while second contact plugs **18** are formed through the first insulating layer **16** to reach the respective drain regions **13**.

20 Capacitors **20** are respectively formed over the first contact plugs **17**. Each of the capacitors **20** includes: a lower electrode **21**; a ferroelectric film **22** and an upper electrode **23** in this order from below. In this case, the ferroelectric films **22** of this embodiment are self-aligned to, i.e., are selectively grown on, the respective lower electrodes **21**. The upper electrodes **23** also serve as a cell plate.

25 Bit lines **24** are formed in upper parts of the first insulating layer **16** to be

electrically connected to the respective second contact plugs **18**. A second insulating layer **25** is formed to fill in the gaps surrounded by the upper faces of the bit lines **24** and the respective sides of the lower electrodes **21** and the ferroelectric films **22**. A third insulating layer **26** is formed on the upper electrode **23**.

5 As an example of the structure of the capacitors **20**, each of the lower electrodes **21** and the upper electrode **23** may be made of platinum (Pt) with a thickness of about 200 nm, and the ferroelectric films **22** may be made of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ with a thickness of about 200 nm.

Hereinafter, a method for forming the capacitors **20** thus configured, especially the
10 ferroelectric films, will be described with reference to FIGS. **2A** and **2B**.

Examples of methods for selectively growing the ferroelectric films **22** on the respective lower electrodes **21** include a method of forming ion clusters in a source gas for the ferroelectric films **22**.

Firstly, a substrate **10** in which selective transistors (not shown) and a first
15 insulating layer **16** have been formed is prepared. Although not shown, first and second contact plugs have been formed in the first insulating layer **16**.

As shown in FIG. **2A**, the substrate **10** is electrically grounded, and then is placed in a heating system (not shown) within a reaction chamber containing a source gas **50**. The source gas **50** is a source gas for use in a metal organic chemical vapor deposition
20 (MOCVD) process, for example. The source gas **50** that has been gasified into organic metal molecules is supplied to the reaction chamber.

In this case, the source gas **50** is passed through ionization apparatus including, for example, a corona tube (not shown) before being supplied to the reaction chamber. In this way, the source gas **50** is ionized to be positively charged ion clusters. The source gas **50**
25 in the state of ion clusters is unstable with respect to energy, so that the source gas **50** tends

to be stabilized by receiving electrons.

Accordingly, the source gas **50** in the state of ion clusters is stabilized by receiving electrons from the lower electrodes **21** that are electrically connected to the grounded substrate **10**, and then the source gas **50** is thermally decomposed. In this way, ferroelectric formation films **22a** start their selective growths on the respective lower electrodes **21**. In this case, the process in which the ion clusters in the source gas **50** agglomerate on the lower electrodes **21** includes the case of self-organization, i.e., the case where the ion clusters agglomerate in the manner of self-assembly because of chemical affinity among identical molecules or clusters.

Therefore, if the lattice constant of crystals in the surfaces of the lower electrodes **21** is selected such that the lattice constant thereof is substantially the same as that of the ferroelectric formation films **22a**, the ferroelectric formation films **22a** are epitaxially grown on the respective lower electrodes **21** so that the resultant ferroelectric formation films **22a** are made of a single crystal or a single domain.

The ion clusters in the material gas **50** do not agglomerate on the region of the first insulating layer **16** other than the lower electrodes **21**. Accordingly, the ion clusters in the material gas **50** are not thermally decomposed in the region other than the region on the lower electrodes **21**.

As a result, as shown in FIG. **2B**, the ferroelectric formation films **21a** grow only on the lower electrodes **21**, thereby obtaining desired ferroelectric films **22**.

The ferroelectric films **22** are preferably grown such that the ferroelectric films **22** are aligned to the respective lower electrodes **21** vertically to the surfaces of the lower electrodes **21** and have a single crystal structure as a crystal orientation which exhibits a relatively strong polarization.

Thereafter, although not shown, a second insulating layer **25** is deposited to cover

the lower electrodes **21** and the ferroelectric films **22**, and then is subjected to chemical mechanical polishing to be planarized such that the surfaces of the ferroelectric films **22** are exposed.

Subsequently, an upper electrode formation film is deposited by a vapor deposition process or a sputtering process over the second insulating layer **25** including the ferroelectric films **22**. Thereafter, an upper electrode **23** having the shape of a cell plate is patterned out of the upper electrode formation film. Then, a third insulating layer **26** is formed to cover the upper electrode **23**, thereby completing a memory device shown in FIG. 1.

In the first embodiment, the ferroelectric films **22** serving as capacitive films for the capacitors **20** is made of a single crystal and has a crystal orientation in which an electric field is applied in the direction for exhibiting a relatively strong polarization. Accordingly, as shown in FIG. 3, hysteresis characteristics according to the present invention as indicated by the solid line are remarkably improved in response, as compared to those of polycrystalline ferroelectric films according to prior art as indicated by the broken line.

In addition, since the ferroelectric films **22** constituting the capacitors **20** are selectively formed on the respective lower electrodes **21**, being self-aligned thereto, no etching for patterning is needed. Accordingly, no damage resulting from etching is created in the ferroelectric films **22**, thus ensuring strong polarization. As a result, even downsized memory cells remarkably improves their characteristics in writing and reading data.

In this embodiment, a vapor phase process using the source gas **50** in the state of ion clusters is used for forming the ferroelectric films **22**. However, the present invention is not limited to this process and may use a long throw sputtering process or a deposition process using a hydrothermal liquid phase.

EMBODIMENT 2

Hereinafter, a second embodiment of the present invention will be described with reference to the drawings.

FIG. 4 shows a cross-sectional structure of a memory array which is a main portion of a memory device according to the second embodiment. In the second embodiment, memory cell array is configured by memory cells arranged three-dimensionally, i.e., stacked as two layers, so as to increase the density in the arrangement of the memory cells. In FIG. 4, each member already shown in FIG. 1 is identified by the same reference numeral and the description thereof will be omitted herein.

As shown in FIG. 4, a peripheral circuit portion 40 including selective transistors 15 and first and second capacitor array layers 41 and 42 each including a plurality of capacitors arranged in an array are formed in this order over a substrate 10.

A first cell plate line 32A is formed between the peripheral circuit portion 40 and the first capacitor array layer 41 with a second insulating layer 31 interposed between the first cell plate line 32A and the peripheral circuit portion 40.

A plurality of lower electrodes 21 are selectively formed over the first cell plate line 32A with first semiconductor thin films 33A of platinum with a thickness of, for example, about 200 nm interposed therebetween. In this way, the first cell plate line 32A, the first semiconductor thin films 33A and the lower electrodes 21 are connected in series, thereby forming bidirectional Schottky barrier diodes 30A of a metal-semiconductor-metal multilayer type.

Ferroelectric films 22 are selectively epitaxially grown only on the respective upper surfaces of the lower electrodes 21 by the same process as in the first embodiment.

Now, other members are described in accordance with the fabrication process. A third insulating layer 34 is formed to cover the ferroelectric films 22, and then is planarized

by polishing until the surfaces of the ferroelectric films **22** are exposed. Thereafter, upper electrodes **23** are formed by a vapor deposition process or a sputtering process on the planarized surface of the second insulating layer **34** including the ferroelectric films **22**, and then the upper electrodes **23** are patterned into desired shapes. Subsequently, a fourth
5 insulating layer **35** is formed on the third insulating layer **34** to cover the upper electrodes **23**, thereby completing a first capacitor array layer **41**.

Then, after the upper surface of the fourth insulating layer **35** has been planarized, a second cell plate line **32B** is formed on the fourth insulating layer **35**. Thereafter, a second capacitor array layer **42** is formed on the second cell plate line **32B**, in the same manner as
10 for the first capacitor array layer **41**.

Specifically, second semiconductor thin films **33B** and lower electrodes **21** are stacked on the second cell plate line **32B**, and then are patterned into desired shapes, thereby forming a plurality of second bidirectional Schottky barrier diodes **30B** made of the second cell plate line **32B**, the second semiconductor thin films **33B** and the lower
15 electrodes **21**. Thereafter, in the manner described above, ferroelectric films **22** are selectively epitaxially grown only on the lower electrodes **21**.

Subsequently, the gaps between the side surfaces of the second semiconductor thin films **33B**, lower electrodes **21** and ferroelectric films **22** are filled with a fifth insulating layer **36**, and then upper electrodes **23** are processed to connect to the respective
20 ferroelectric films **22**. Lastly, a sixth insulating layer **37** is formed on the surface of the fifth insulating layer **36** including the upper electrodes **23**, thereby completing a second capacitor array layer **42**.

In the second embodiment, with respect to the first capacitor array layer **41**, for example, the first bidirectional Schottky barrier diodes **30A** made up of the first cell plate
25 line **32A**, the first semiconductor thin films **33A** and the lower electrodes **21** function as

selective switching devices for respective memory cells.

Although not shown, a wiring portion where memory cells including the capacitors **20** arranged in the first capacitor array layer **41** are electrically connected to memory cells including the capacitors **20** arranged in the second capacitor array layer **42** is buried
5 between the first and second capacitor array layers **41** and **42**.

In the second embodiment, the capacitor array layer is made of two layers. However, the present invention is not limited to this specific embodiment and three or more layers may constitute the capacitor array layer. In this way, it is possible to arrange the memory cell array three-dimensionally without forming any damaged region in a
10 capacitor film made of a ferroelectric, thus downsizing memory cells as well as increasing the density in the arrangement of the memory cells.

Instead of the second bidirectional Schottky barrier diodes **30B**, a thin film transistor may be used.